

HIGH HARD, STRENGTH AND TOUGH NANO-CRYSTAL METAL BULK  
MATERIAL, AND ITS PREPARATION PROCESS

ART FIELD

5           The present invention relates generally to a metal material, and more particularly to a high hard, strength and tough nano-crystal metal bulk material, and its preparation process.

10                           BACKGROUND OF THE INVENTION

          As the Petch relationship teaches, metal material strength and hardness increase with decreasing crystal grain diameter  $D$ , and such relationships hold as far as  $D$  is at or near a few tens of nm. Thus, reducing crystal grain diameters down to nano-size levels now becomes one of the most important means ever for the reinforcement of metal materials.

          On the other hand, as crystal grain diameters are reduced down to ultra-fine, nano-size levels, most metal materials come to show a unique phenomenon called super-plasticity in a temperature region of higher than  $0.5T_m$  where  $T_m$  is a melting point (K).

          Harnessing that phenomenon enables even materials extremely unsusceptible to plastic processing or the like due to high melting points or temperatures to be deformed and processed at relatively low temperatures.

          There are some reports that regarding magnetic elements such as iron, cobalt and nickel, in nano-order

grain diameter ranges coercive force decreases and soft magnetism improves with decreasing D, which are not found when the crystal grain diameter D is in micron-order ranges.

5           However, the crystal grain diameter D of most metal materials produced by melting are usually on the order of a few microns to a few thousand of microns, and D can hardly be reduced down to the nano-order even by post-treatments. Even with controlled rolling that is an  
10 important micro-processing of steel crystal grains, for instance, the lowest possible limit to grain diameters is of the order of at most 4 to 5  $\mu\text{m}$ . In other words, with such ordinary processes it is impossible to obtain materials whose grain diameters are reduced down to the  
15 nano-size level.

#### DISCLOSURE OF THE INVENTION

The present invention has for its object the provision of satisfactory solutions to the above problems.

20           Basically, the present invention makes use of mechanical milling (MM) or mechanical alloying (MA) of a powder mixture of powders of an elementary or semimetal single metal and powders of other metal additives or the like. The resulting nano-crystal fine powders are refined  
25 by forming-by-sintering or methods using superplasticity in the forming-by-sintering process down to nano-size levels, thereby providing a bulk material having strength (high strength) and hardness (super hardness) close to the

limits achievable with crystal grain diameters reduced down to the nano-size level, and corrosion resistance as well.

Thus, the present invention is concerned with nano-  
5 crystal metal bulk materials as recited below, and their preparation processes.

(1) A high hard, strength and tough nano-crystal metal bulk material, comprising an aggregate of metal  
10 nano-crystal grains, characterized in that a metal oxide or a semimetal oxide exists as a crystal grain growth inhibitor between and/or in said nano-crystal grains.

(2) A high hard, strength and tough nano-crystal metal bulk material, comprising an aggregate of metal  
15 nano-crystal grains, characterized in that a metal nitride or a semimetal nitride exists as a crystal grain growth inhibitor between and/or in said nano-crystal grains.

(3) A high hard, strength and tough nano-crystal metal bulk material, comprising an aggregate of metal  
20 nano-crystal grains, characterized in that a metal carbide or a semimetal carbide exists as a crystal grain growth inhibitor between and/or in said nano-crystal grains.

(4) A high hard, strength and tough nano-crystal metal bulk material, comprising an aggregate of metal  
25 nano-crystal grains, characterized in that a metal silicide or a semimetal silicide exists as a crystal grain growth inhibitor between and/or in said nano-crystal grains.

(5) A high hard, strength and tough nano-crystal metal bulk material, comprising an aggregate of metal nano-crystal grains, characterized in that a metal boride or a semimetal boride exists as a crystal grain growth inhibitor between and/or in said nano-crystal grains.

(6) A high hard, strength and tough nano-crystal metal bulk material, comprising an aggregate of metal nano-crystal grains, characterized in that:

at least two compounds selected from the group consisting of (1) a metal oxide or a semimetal oxide, (2) a metal nitride or a semimetal nitride, (3) a metal carbide or a semimetal carbide, (4) a metal silicide or a semimetal silicide and (5) a metal boride or a semimetal boride exist as a crystal grain grown inhibitor between and/or in said nano-crystal particles.

(7) The high hard, strength and tough nano-crystal metal bulk material according to any one of (1) to (6) above, characterized in that the bulk material comprising an aggregate of metal nano-crystal grains contains nitrogen in an amount of 0.01 to 5.0% by mass.

(8) The high hard, strength and tough nano-crystal metal bulk material according to any one of (1) to (6) above, characterized in that the bulk material comprising an aggregate of metal nano-crystal grains contains nitrogen in an amount of 0.1 to 2.0% by mass.

(9) The high hard, strength and tough nano-crystal metal bulk material according to any one of (1) to (8) above, characterized in that the bulk material comprising

an aggregate of metal nano-crystal grains contains a metal oxide form of oxygen in an amount of 0.01 to 1.0% by mass.

(10) The high hard, strength and tough nano-crystal metal bulk material according to any one of (1) to (9)

5 above, characterized by further comprising a metal element having a stronger chemical affinity for nitrogen than a nano-crystal metal so as to prevent denitrification of the aggregate comprising metal nano-crystal grains in a forming-by-sintering process.

10 (11) The high hard, strength and tough nano-crystal metal bulk material according to any one of (1) to (10) above, characterized in that a nano-crystal metal-forming component is at least one element selected from the group consisting of aluminum, magnesium, zinc, titanium, calcium,  
15 beryllium, antimony, yttrium, scandium, indium, uranium, gold, silver, chromium, zirconium, tin, tungsten, tantalum, iron, nickel, cobalt, copper, niobium, platinum, vanadium, manganese, molybdenum, lanthanum, rhodium, carbon, silicon, boron, nitrogen and phosphor.

20 (12) The high hard, strength and tough nano-crystal metal bulk material according to any one of (1) to (10) above, characterized in that a nano-crystal metal-forming component is a dental platinum-group element.

(13) The high hard, strength and tough nano-crystal  
25 metal bulk material according to any one of (1) to (10) above, characterized in that a nano-crystal material is one or two or more intermetallic compounds selected from the group consisting of  $\text{Ni}_3\text{Al}$ ,  $\text{Fe}_3\text{Al}$ ,  $\text{FeAl}$ ,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ ,

TiAl<sub>3</sub>, ZrAl<sub>3</sub>, NbAl<sub>3</sub>, NiAl, Nb<sub>3</sub>Al, Nb<sub>2</sub>Al, MoSi<sub>2</sub>, Nb<sub>5</sub>Si<sub>3</sub>,  
Ti<sub>5</sub>Si<sub>3</sub>, Nb<sub>2</sub>Be<sub>17</sub>, Co<sub>3</sub>Ti, Ni<sub>3</sub>(Si, Ti), SiC, Si<sub>3</sub>N<sub>4</sub>, AlN, TiNi,  
ZrB<sub>2</sub>, HfB<sub>2</sub>, Cr<sub>3</sub>C<sub>2</sub>, or Ni<sub>3</sub>Al-Ni<sub>3</sub>Nb.

(14) The high hard, strength and tough nano-crystal  
5 metal bulk material according to any one of (1) to (13)  
above, characterized in that the metal nano-crystal grains  
have been obtained by mechanical milling (MM) or  
mechanical alloying (MA) using a ball mill or the like.

(15) A process for preparing a nano-crystal metal  
10 bulk material, characterized by involving steps of:

applying mechanical alloying (MA) to respective fine  
powders of nano-crystal metal-forming components, using a  
ball mill or the like, thereby preparing fine powders of a  
nano-crystal metal, and

15 applying to said fine powders of a nano-crystal  
metal hot forming-by-sintering treatment such as sheath  
rolling, spark plasma sintering or extrusion, or explosive  
forming, thereby obtaining a high hard, strength and tough  
metal bulk material.

20 (16) A process for preparing a nano-crystal metal  
bulk material, characterized by involving steps of:

mixing respective fine powders of nano-crystal  
metal-forming components together with a substance that  
becomes a nitrogen source,

25 applying mechanical alloying (MA) to the resulting  
mixture, using a ball mill or the like, thereby preparing  
high nitrogen-concentration, nano-crystal metal powders,  
and

applying to said metal powders hot forming-by-sintering treatment such as sheath rolling, spark plasma sintering or extrusion, or explosive forming, thereby obtaining a high hard, strength and tough metal bulk material.

(17) The process for preparing a nano-crystal metal bulk material according to (16) above, characterized in that the substance that becomes a nitrogen source is a metal nitride.

(18) The process for preparing a nano-crystal metal bulk material according to (16) above, characterized in that the substance that becomes a nitrogen source is  $N_2$  gas or  $NH_3$  gas.

(19) The process for preparing a nano-crystal metal bulk material according to any one of (15) to (18) above, characterized in that an atmosphere in which mechanical milling or mechanical alloying is applied is any one gas selected from the group consisting of (1) an inert gas such as argon gas, (2)  $N_2$  gas, and (3)  $NH_3$  gas or (4) a mixed gas of two or more gases selected from (1) to (3).

(20) The process for preparing a nano-crystal metal bulk material according to (19) above, characterized in that an atmosphere in which mechanical milling or mechanical alloying is applied is an atmosphere of a gas with some reducing substance such as  $H_2$  gas added thereto.

(21) The process for preparing a nano-crystal metal bulk material according to (15) or (16) above, characterized in that an atmosphere in which mechanical

milling or mechanical alloying is applied is a vacuum, a vacuum atmosphere with some reducing substance such as  $H_2$  gas added to a vacuum or a reducing atmosphere.

(22) The process for preparing a nano-crystal metal bulk material according to any one of (16) to (21) above, characterized by involving steps of:

mixing the respective fine powders of nano-crystal metal-forming components and 1 to 10% by volume of a metal nitride or 0.5 to 10% by mass of a nitrogen affinity metal having a stronger chemical affinity for nitrogen than for a nano-crystal metal together with a substance that becomes a nitrogen source,

applying mechanical alloying (MA) to the resulting mixture, using a ball mill or the like, thereby preparing high-nitrogen nano-crystal metal powders, and

applying to said metal powders hot forming-by-sintering treatment such as sheath rolling, spark plasma sintering or extrusion or explosive forming, wherein said additive nitride is dispersed or a nitride, carbo-nitride or the like of said metal element is precipitated or dispersed in a mechanical alloying (AM) process or a forming-by-sintering process of mechanically alloyed (MA) powders, thereby obtaining a high hard, strength and tough metal bulk material.

(23) The process for preparing a nano-crystal metal bulk material according to any one of (15) to (22) above, characterized in that a nano-crystal metal has a blending composition containing 0 to 40% by mass of other element,



and the forming-by-sintering is carried out at a temperature that is at least 10% lower than a melting point or melting temperature.

(24) A process for preparing a high hard, strength  
5 and tough nano-crystal steel bulk material, characterized by involving steps of:

applying mechanical alloying (MA) to respective  
powders of nano-crystal steel-forming components using a  
ball mill or the like, thereby preparing nano-crystal  
10 steel powders, and

applying to said steel powders forming-by-sintering  
treatment such as spark plasma sintering, hot pressing,  
extrusion or rolling or explosive forming at or near a  
superplasticity-inducing temperature.

15 (25) A process for preparing a high hard, strength  
and tough nano-crystal cast iron bulk material,  
characterized by involving steps of:

applying mechanical alloying (MA) to respective  
powders of nano-crystal cast iron-forming components using  
20 a ball mill or the like, thereby preparing nano-crystal  
cast iron powders, and

applying to said cast iron powders forming-by-  
sintering treatment such as spark plasma sintering, hot  
pressing, extrusion or rolling or explosive forming at or  
25 near a superplasticity-inducing temperature.

(26) A process for preparing a high hard, strength  
and tough nano-crystal steel formed material,  
characterized by involving steps of:

applying mechanical alloying (MA) to respective powders of nano-crystal steel-forming components using a ball mill or the like, thereby preparing nano-crystal steel powders,

5        applying to said steel powders forming-by-sintering treatment such as spark plasma sintering, hot pressing, extrusion or rolling or explosive forming, thereby obtaining a steel bulk material, and

forming said steel bulk material at or near a super-  
10    plasticity-inducing temperature.

(27) A process for preparing a high hard, strength and tough nano-crystal cast iron formed material, characterized by involving steps of:

applying mechanical alloying (MA) to respective  
15    powders of nano-crystal cast iron-forming components using a ball mill or the like, thereby preparing nano-crystal cast iron powders,

applying to said cast iron powders forming-by-sintering treatment such as spark plasma sintering, hot  
20    pressing, extrusion or rolling or explosive forming, thereby obtaining a cast iron bulk material, and

forming said cast iron bulk material at or near a superplasticity-inducing temperature.

25        According to the invention as defined above, as either mechanical milling (MM) or mechanical alloying (MA) is applied to a powdery material of a single metal with other element added thereto, it is formed into powders

having an ultra-fine crystal grain structure. By the forming-by-sintering of those powders at a temperature that is at most 10% lower than the melting point or melting temperature of those powders, the metal bulk material can be easily prepared.

As mechanical alloying (MA) is applied to a powdery mixture of powders of a practical single metal such as iron, cobalt, nickel, and aluminum with carbon, niobium, titanium or the like added thereto, there is obtained a more ultra-fine crystal grain structure. Such forming-by-sintering as mentioned above readily gives a bulk material having a nano-crystal grain structure, which is much higher than that obtained by melting in terms of strength and hardness.

By suitable selection of crystal grain size, composition, or the like, superplasticity is induced in the nano-crystal material, and this phenomenon can be effectively applied to the forming-by-sintering process of MA powders.

#### BRIEF EXPLANATION OF THE DRAWINGS

Fig. 1 is illustrative of the mean crystal grain diameters of each element upon 50-hour mechanical alloying (MA) of powders of iron, cobalt and nickel with other element (A) added thereto in an amount of 15 at%, as used in one specific example of the invention.

Fig. 2 is illustrative in graph of the relationships between the crystal grain diameter  $D_{Fe}$  of iron used in one

specific example of the invention and the logarithm  $\log \beta$  of grain boundary segregation factor  $\beta$  of the solute element added.

Fig. 3 is illustrative in graph of the relationships between the crystal grain diameter  $D_{Co}$  of cobalt used in one specific example of the invention and the logarithm  $\log \beta$  of grain boundary segregation factor  $\beta$  of the solute element added.

Fig. 4 is illustrative in graph of the relationships between the crystal grain diameter  $D$  of the sample as used in one specific example of the invention and the amount of tantalum added (at%).

#### BEST MODE FOR CARRYING OUT THE INVENTION

Some embodiments of the invention are now explained. In one embodiment of the invention, mechanical milling (MM) or mechanical alloying (MA) is applied to elementary powders of single metals such as iron, cobalt, nickel, aluminum and copper with or without other elements added thereto, using a ball mill or the like at room temperature in an argon gas or other atmosphere.

The mechanically milled or mechanically alloyed powders are easily reduced down to a crystal grain diameter of about 10 to 20 nm by mechanical energy applied by ball milling. For instance, iron reduced down to a grain diameter of about 25 nm has a Vickers hardness of about 1,000.

Then, the thus mechanically milled or mechanically alloyed powders are vacuum charged in a stainless steel tube (sheath) of about 7 mm in inside diameter, for forming-by-sintering by means of sheath rolling using a rolling machine at a temperature that is at most 10% lower than the melting point or melting temperature. In this way, for instance, an iron sheet of at least 1.5 GPa in offset yield strength and about 1.5 mm in thickness can be easily prepared.

10 Further, if mechanical alloying (MA) is applied to a powdery mixture comprising elementary powders of iron, cobalt, nickel, aluminum, copper and so on with other elements such as carbon, niobium and titanium added thereto in an amount of about 0.5 to 15% by mass, using a ball mill or the like, the powders are much further  
15 reduced in the MA process down to more ultra-fine levels, i.e., crystal grains of a few nano-order level.

If the amount of a metal or semimetal oxide form of oxygen inevitably entrapped in the powders that are  
20 undergoing mechanical alloying (MA) is usually regulated to up to about 0.5% by mass, it is then possible to prevent coarsening of crystal grains in the forming-by-sintering process. To enhance such coarsening-prevention effects, it is desirable to add 1 to 10% by volume,  
25 especially 3 to 5% by volume of a crystal grain dispersant such as AlN, and NbN to the mechanically alloyed (MA) powders.

In the invention, mechanical milling (MM) or

mechanical alloying (MA) is applied to powders of single metals such as iron, cobalt, nickel, aluminum, coppers with or without other elements added thereto to prepare powders having a nano-size crystal grain structure. Then, as the metal powders are formed by forming-by-sintering such as sheath rolling or extrusion, the amount of a metal oxide form of oxygen that is inevitably formed during the mechanical milling (MM) or mechanical alloying (MA) process is regulated to up to about 0.5% (by mass), so that any coarsening of crystal grains is held back by the pinning effect of that oxide on crystal grain boundaries. It is thus possible to achieve effective preparation of nano-crystal materials.

15

## EXAMPLES

Examples of the invention are now explained with reference to the accompanying drawings.

### Example 1

Fig. 1 is illustrative of changes in the mean crystal grain diameter of each mechanically alloyed element, that is, iron, cobalt and nickel when a 50-hour mechanical alloying (MA) was applied to an elementary powder mixture having an  $M_{85}A_{15}$  (at%) (M is iron, cobalt or nickel), which comprised powders of the elements iron, cobalt and nickel with the addition thereto of 15 at% of carbon (C), niobium (Nb), tantalum (Ta), titanium (Ti) and so on as other elements (A).

In Fig. 1,  $D_{Fe}$ ,  $D_{Co}$  and  $D_{Ni}$  are the mean crystal grain

diameter (nm) of the mechanically alloyed iron, cobalt, and nickel, respectively. From Fig. 1, it has been found that the reduction of crystal grain diameters of each of the elements iron, cobalt and nickel can be more  
5 effectively promoted by mechanical alloying with the addition thereto of carbon, niobium, tantalum, titanium and so on, all the three elements being refined down to grain diameters of a few nano-orders.

It has also been found that the reduction of crystal  
10 grains of copper, aluminum, and titanium, too, is promoted by the addition thereto of other elements, and that carbon, phosphor and boron are particularly effective as such elements. It is here noted that the other elements used include carbon (C), niobium (Nb), tantalum (Ta), phosphor  
15 (P), boron (B) or the like, and that the data about nitrogen N are directed to iron alone.

Fig. 2 is illustrative in graph of the relationships between the crystal grain diameter  $D_{Fe}$  of iron and the common logarithm  $\log \beta$  of grain boundary segregation  
20 factor  $\beta$  of the additive element A in iron.

The additive element A, for instance, includes carbon (C), nitrogen (N), tantalum (Ta), and vanadium (V).

From Fig. 2, it has been found that the larger the value of  $\log \beta$ , the more enhanced the effect on the  
25 refinement of crystal grains in the MA process is.

Fig. 3 is illustrative in graph of the relationships between the crystal grain diameter  $D_{Co}$  of cobalt and the

common logarithm  $\log \beta$  of grain boundary segregation factor  $\beta$  of the additive element A in cobalt.

The additive element A, for instance, includes carbon (C), niobium (Nb), and tantalum (Ta).

- 5        From Fig. 3, it has been found that the larger the value of  $\log \beta$ , the more enhanced the effect on the refinement of crystal grains in the MA process is.

#### Example 2

- Fig. 4 is illustrative in graph of the relationships  
10    between the mean crystal grain diameter  $D$  (nm) of an  $\text{Fe}_{64-y}\text{Cr}_{18}\text{Ni}_8\text{Ta}_y\text{N}_{10}$  (at%) where  $y = 0$  to 15, obtained by a 100-hour MA treatment of a powder mixture of elements iron, nickel and tantalum with the addition thereto of iron nitride, and the amount of tantalum added  $y$  (at%).

- 15        From Fig. 4, it has been found that the marked grain refinement effect of the additions elements A having the large value of the grain boundary segregation factor  $\beta$  in the binary Fe and A materials is similarly seen in the multicomponent materials based on component Fe as well.

#### 20    Example 3

- A powder sample of  $\text{Fe}_{99.8}\text{C}_{0.2}$  (% by mass) was obtained by the mechanical alloying (MA) of a powder mixture of elements iron and carbon for 200 hours. Then, the sample was vacuum charged in a stainless steel tube (sheath).  
25    Consolidation (i.e., sintering) of the vacuum charged powder sample was performed by sheath rolling (SR) at a temperature of  $900^\circ\text{C}$ , obtaining an SR formed product (bulk



material) as shown in Table 1.

Table 1

Mean crystal grain diameter D, Vickers hardness Hv and the value of oxygen upon analysis of Fe<sub>99.8</sub>Co<sub>0.2</sub> (% by mass) bulk material obtained by 900°C-sheath rolling (SR) of powder material mechanically alloyed from a powder mixture of elements iron and carbon

Sample	D (nm)	Hv	Oxygen % by mass
SR formed material*	23	980	0.485

The value of D was calculated from Scherrer's equation, and \* indicates that the material thickness was about 1.4 mm.

From Example 3 and Table 1, it has been found that according to the invention, the Vickers hardness Hv of the formed material is enhanced by the reduction of crystal grains down to the nano-order, exceeding that of a hardened material having a high-carbon steel's martensite structure.

#### Example 4

Alloy powders of (a) Fe<sub>86</sub>Cr<sub>13</sub>N<sub>1</sub> (% by mass) and (b) Fe<sub>69.25</sub>Cr<sub>20</sub>Ni<sub>8</sub>Ta<sub>2</sub>N<sub>0.75</sub> (% by mass) were prepared by mechanical alloying (MA) of powder mixtures comprising powders of elements iron, chromium, nickel and tantalum and iron nitride (containing 8.51% by mass of nitrogen), using a ball mill in an argon atmosphere.

Then, these alloy powders were charged in a graphite

die of 40 mm in inside diameter, and the die was placed in a vacuum for spark plasma sintering (SPS) at 900°C, after which hot rolling was further applied to the sintered product at the same temperature, annealed at 1,150°C for 15 minutes, and finally cooled with water. Table 2 shows the mean crystal grain diameter d, hardness Hv, tensile strength  $\sigma_B$ , elongation  $\delta$  and the value of oxygen and nitrogen upon analysis of the rolled/annealed products.

10

Table 2

Mean crystal grain diameter d, hardness Hv, tensile strength  $\sigma_B$ , elongation  $\delta$  and the value of oxygen and nitrogen upon analysis of the formed materials (spark plasma sintering (vacuum, 900°C) plus rolling (vacuum, 900°C) plus annealing (1,150°C×15 minutes/water cooling)), obtained from mechanically alloyed (MA) powder samples of (a)  $\text{Fe}_{86}\text{Cr}_{13}\text{N}_1$  (% by mass) and (b)  $\text{Fe}_{69.25}\text{Cr}_{20}\text{Ni}_8\text{Ta}_2\text{N}_{0.75}$  (% by mass)

20

Sample	d (nm)		Hv	$\sigma_B$ MPa	$\delta$ %	Oxygen* % by mass	Nitrogen % by mass
a	A	B					
	20	200	770	2,200	15	0.502	1.02
b	17	150	680	2,050	20	0.544	0.746

A: MA powder sample

25 - B: formed material sample

\*: the value of oxygen of the feed powders used for MA upon analysis was 0.23 to 0.28% by mass.

From Table 2, it has been found that although there is some considerable growth of crystal grains during both the hot forming-by-sintering process and the annealing process, yet both the formed samples keep their nano-size level crystal grain structure. This could be due to the pinning of crystal grain boundaries by metal or semimetal oxides of oxygen contained in the mechanically alloyed (MA) alloy powders.

It has also been found that through both the effects of nitrogen solid solution and ultra-fine crystal grains, both the alloys are much more improved in terms of hardness Hv and tensile strength  $\sigma_B$ .

For making use of superplasticity induced by forming-by-sintering in powder materials, it is of the most importance that crystal grains therein be reduced down to a ultra-fine level, and that growth of crystal grains during the deformation process due to superplasticity be reduced as much as possible.

According to the invention, forming-by-sintering processes harnessing superplasticity are easily achievable, because powders of nano-size ultra-fine crystal grains are easily obtainable by mechanical alloying (MA) of feed powders, and because metal oxides resulting inevitably from that mechanical alloying (MA) prevent growth of grains during forming-by-sintering processes.

Examples of forming-by-sintering making use of superplasticity according to the invention are now

explained with reference to Tables 3, 4 and 5.

#### Example 5

According to the invention, a superplasticity-harnessing forming-by-sintering process was effectively  
5 achieved with powders obtained by mechanical alloying (MA) of a carbon steel material having a hyper-eutectoid steel composition with a carbon content of 0.765 to 2.14% by mass in particular. One example is given below.

Alloy powders having a hyper-eutectoid steel  
10 composition of  $\text{Fe}_{96.1-x}\text{C}_{1.5}\text{Cr}_{1.7}\text{Mn}_{0.5}\text{N}_{0.2}\text{Si}_x$  (% by mass) where  $x = 1$  to 3 were prepared by ball mill mechanical alloying (MA, an argon gas atmosphere) of a powder mixture of powdery elements iron, carbon, chromium, manganese and silicon with iron nitride having a nitrogen content of  
15 8.51% by mass. The powders were charged in a graphite die of 40 mm in inside diameter for a 15-minute hot pressing in a vacuum and at 750°C and a pressure of 60 MPa, thereby obtaining a pre-sintered mass of 40 mm in diameter and about 5 mm in thickness.

20 Then, a given compression load was applied to the pre-sintered mass at 800°C and a strain rate of  $10^{-4}$ /sec. for 30 minutes in its thickness direction to obtain a formed-by-sintering product. Set out in Table 3 are the mean crystal grain diameter  $d$ , hardness  $H_v$ , tensile  
25 strength  $\sigma_B$ , elongation  $\delta$  and the values of oxygen and nitrogen upon analysis of the formed product at different Si concentrations ( $x$ , % by mass).

It is here noted that nitrogen was incorporated in the present alloy sample for the purpose of enhancing its strength.

From Table 3 and the value of ordinary-temperature  
5 hardness Hv, it has been found that the sintering process of these samples at 800°C comes to be more effective from the Si concentration of 2% by mass or higher.

The concentration of Si should preferably be from 2.0 to 3.5% by mass.

10

Table 3

Relationships between the concentration of Si of  $\text{Fe}_{96.1-x}\text{C}_{1.5}\text{Cr}_{1.7}\text{Mn}_{0.5}\text{N}_{0.2}\text{Si}_x$  (% by mass,  $x = 1$  to 3) samples obtained by mechanical alloying (MA) and forming-by-sintering, densification during the forming-by-sintering process and the mechanical properties of the formed samples

Si concentration (x)		1.0	1.5	2.0	2.5	3.0
(% by mass)						
10	$d^*$ (nm)	4,400	3,200	290	240	210
	Hv	200	230	570	610	650
	$\sigma_B$ (MPa)	-	-	1,220	1,350	1,430
	$\delta$ (%)	-	-	24	15	12
	Oxygen (% by mass)	0.445	0.506	0.496	0.431	0.543
15	<u>Nitrogen (% by mass)</u>	<u>0.202</u>	<u>0.198</u>	<u>0.207</u>	<u>0.210</u>	<u>0.204</u>

\* indicates that the MA powders at each concentration  $x$  have a mean crystal grain diameter of 7 to 20 nm.

#### Example 6

20 According to the invention, a superplasticity-harnessing forming-by-sintering process was effectively achieved with powders obtained by mechanical alloying (MA) of a material having a plain cast iron composition, and a white cast iron composition with a carbon content of 2.2 to 4.3% by mass. One example is given below.

As in Example 5, alloy powders having a cast iron composition of  $\text{Fe}_{94.3}\text{C}_{3.5}\text{Cr}_2\text{N}_{0.2}$  (% by mass) were prepared by.

mechanical alloying (MA) of a powder mixture of powdery elements iron, carbon and chromium with iron nitride having a nitrogen content of 8.51% by mass. The powders were charged in a graphite die of 40 mm in inside diameter  
5 for a 15-minute hot pressing in a vacuum and at 700°C and a pressure of 60 MPa, thereby obtaining a pre-sintered mass of 40 mm in diameter and 5 mm in thickness.

Then, a given compression load was applied to the pre-sintered mass at a strain rate of  $10^{-4}$ /sec. for 30  
10 minutes in its thickness direction at temperatures of 550°C, 600°C, 650°C, 700°C and 750°C to obtain a formed-by-sintering product. Set out in Table 4 are the mean crystal grain diameter  $d$ , hardness  $H_v$ , tensile strength  $\sigma_B$ , elongation  $\delta$  and values of oxygen and nitrogen upon  
15 analysis of the formed product at different forming temperatures  $T$ .

Table 4

Forming-by-sintering temperatures of mechanically alloyed  
(MA) powder alloy  $\text{Fe}_{94.3}\text{C}_{3.5}\text{Cr}_2\text{N}_{0.2}$  (% by mass) and  
mechanical properties of the formed products

5	T (°C)	550	600	650	700	750
	d (nm)	2,080	2,510	150	230	270
	Hv	145	210	810	740	690
	$\sigma_B$ (MPa)	-	-	1,610	1,530	1,380
	$\delta$ (%)	-	-	10	17	23
10	Oxygen (% by mass)	0.503	0.469	0.457	0.432	0.425
	Nitrogen (% by mass)	0.205	0.208	0.201	0.204	0.207

From Table 4 and the ordinary-temperature hardness,  
it has been found that the sintering process of each  
15 sample comes to be more effective from the temperature of  
650°C or higher.

#### Example 7

As in Example 6, alloy powders of (a)  $\text{Ti}_{88}\text{Ta}_6\text{Nb}_4\text{Fe}_2$  (%  
by mass), (b)  $\text{Ti}_{88}\text{Nb}_6\text{Zr}_4\text{Fe}_2$  (% by mass) and (c)  $\text{Ti}_{88}\text{Zr}_6\text{Ta}_4\text{Fe}_2$   
20 (% by mass) were prepared by mechanical alloying (MA) of  
powder mixture of elementary powders titanium, tantalum,  
niobium and zirconium, and iron. The powders were charged  
in a graphite die of 40 mm in inside diameter for a 15-  
minute hot pressing in a vacuum and at 850°C and a  
25 pressure of 60 MPa, thereby obtaining a pre-sintered mass  
of 40 mm in diameter and 5 mm in thickness.

Then, a given compression load was applied to the



pre-sintered mass at a strain rate of  $10^{-4}$ /sec. for 15 minutes in its thickness direction at varying temperatures to find a superplasticity start temperature  $T_{sp}$  at which the normal-temperature hardness of the pre-sintered mass started to rise sharply. The results are reported in Table 5.

Table 5

Mechanical properties of formed products obtained from mechanically alloyed (MA) (a)  $Ti_{88}Ta_6Nb_4Fe_2$  (% by mass), (b)  $Ti_{88}Nb_6Zr_4Fe_2$  (% by mass) and (c)  $Ti_{88}Zr_6Ta_4Fe_2$  (% by mass) alloy powders and softening (superplasticity) start temperatures thereof during the forming process

Sample	$d^*$	Hv	$\sigma_B$	$\delta$	$T_{sp}$	Oxygen
	nm		MPa	%	$^{\circ}C$	% by mass
a	150	720	1,700	10	910	0.551
b	190	650	1,610	14	890	0.603
c	240	590	1,540	22	850	0.675

\* indicates that the mean crystal grain diameter in the MA powders was 14 to 20 nm.

Specifically, Table 5 shows the mean crystal grain diameter  $d$ , hardness Hv, tensile strength  $\sigma_B$ , elongation  $\delta$  and the value of oxygen upon analysis of the formed product obtained by the application of a given compression load at a temperature  $50^{\circ}C$  higher than  $T_{sp}$  and a strain rate of  $10^{-4}$ /sec. for 30 minutes.

From Example 5 (Table 3), Example 6 (Table 4) and Example 7 (Table 5), it has been found that with the formed-by-sintering product comprised of nano-crystals, there is a specific temperature at which super-plasticity occurs depending on the size, composition, etc. of crystal grains, and superplasticity induced at or near that temperature allows crystal grains to be more effectively bonded together at nano-size levels during the forming-by-sintering process, contributing to an extremely high hardness of the bulk material at ordinary temperature.

Referring now to Example 5 (Table 3), the more effective sintering process at the Si concentration of more than 2% could be due to the effect of Si on noticeable prevention of grain growth under the compression load.

From Example 7 (Table 5), it has been found that according to the invention, even alloys having a high melting temperature, like Ti alloys, can be refined by MA to powders composed of nano-size crystal grains, and that bulk materials can be prepared from such alloys by way of a forming-by-sintering process at relatively low temperatures.

#### Example 8

Alloy powders of mechanically alloyed (MA) (a)  $\text{Al}_{93.5}\text{Cu}_6\text{Zr}_{0.5}$  (% by mass), (b)  $\text{Cu}_{87}\text{Al}_{10}\text{Fe}_3$  (% by mass) and (c)  $\text{Ni}_{48.25}\text{Cr}_{39}\text{Fe}_{10}\text{Ti}_{1.75}\text{Al}_1$  (% by mass) exhibit super-plasticity at or near 430°C, 750°C and 770°C, respectively,

and each temperature was about 50°C lower than the superplasticity start temperature of an alloy prepared by melting.

Chief reasons for that could be that the crystal  
5 grains in the nano-crystal material of the invention are reduced down to ultra-fine levels, and the metal oxide or the like present between and/or in nano-crystal grains behaves as an effective crystal grain growth inhibitor.

In accordance with the invention, for instance,  
10 hard-to-process materials such as cast iron, high-melting point materials or titanium alloys that have only limited applications because of their brittleness, too, can be converted into high hard, strength and tough materials that are never achievable by the prior art by way of the  
15 preparation of nano-crystal powders by mechanical alloying (MA) and the application thereto of a forming-by-sintering process harnessing superplasticity. Thus, the present invention can successfully provide an unheard-of, high hard, strength and tough material (a bulk material  
20 comprising an aggregate of nano-crystal grains), as explained with reference to Examples 6 and 7.

#### POSSIBLE APPLICATIONS OF THE INVENTION TO THE INDUSTRY

The nano-crystal metal bulk materials obtained  
25 according to the inventions are well fit for such applications as given below.

(1) Bearings

When the nano-crystal metal bulk material of the invention is used for the rotary parts of bearings, the amount of that material used can be much reduced because of its strength properties, so that not only can the material used be greatly saved, but it is also possible to achieve great power savings during bearing operation through a large lowering of centrifugal force of the moving part of the bearing.

## 10 (2) Gears

Metal materials used for most of gears must meet contradictory requirements of giving wear resistance to the surface (tooth face) portion of, and strong toughness to the interior of, one single gear, resulting in the need of surface hardening treatment that relies on a sophisticatedly combined technique and skill comprising carburizing to the tooth face portion, etc. and hardening and tempering. When the super hard and tough nano-crystal metal bulk prepared by extrusion according to the invention is used for this purpose, however, such surface hardening treatment can be dispensed with.

## (3) Tools for Hot Processing and Extrusion

Hardened and tempered materials often used as high-temperature cutting tools, for instance, molybdenum based high-speed steel materials, have the nature of softening rapidly at a temperature higher than near 400°C owing to the fact that the matrix is composed of a tempered

martensite phase that becomes instable upon temperature rises. However, the nano-crystal metal bulk material of the invention, because its matrix is composed in itself of a stable phase and so free from rapid softening at such a  
5 temperature region, could be used as more favorable materials for tools dedicated to hot processing.

The nano-crystal metal bulk material of the invention, also because its matrix is relatively thermally stable, could be more effectively used for extrusion tools  
10 exposed to vigorous thermal changes during use.

#### (4) Medical Tools or the Like

Unlike nickel-containing chromium-nickel based austenite stainless steels, titanium based bulk materials or high-nitrogen chromium-manganese based austenite steels  
15 cause no inflammation to the skin or skin diseases, and so they are potentially promising as surgeon's knives, medical low-temperature tools, sharp-edged tools like general-purpose knives, tools so on.